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REVIEW OF DUCTILIZING OF GROUP VIA ELEMENTS BY RHENIUM AND OTHER SOLUTES

by William D. Klopp

Lewis Research Center

Cleveland, Ohio

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ABSTRACT

The ductility of Group VIA alloys containing rhenium and other solutes from Groups VIIA and VIIIA was reviewed. The rhenium ductilizing effect, found in Group VIA alloys containing 25 to 35 at. % Re, is promoted by other solutes from Group VIIA and the early portions of Group VIIIA. The hardness minimums and lowered ductile-brittle transition temperatures observed in dilute Mo-Re and W-Re alloys are attributed to solution softening. This phenomenon occurs at low temperatures and is common to many dilute body-centered-cubic alloys containing substitutional solutes.

CONTENTS

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SUMMARY

The properties of Group VIA-base alloys with rhenium (Re) and with other solutes from Groups VIIA and VIIIA were reviewed to determine correlations pertinent to the lowered ductile-brittle transition temperatures observed in both near-saturated and dilute Group VIA-Re alloys. The rhenium ductilizing effect, originally observed in chromium (Cr), molybdenum (Mo), and tungsten (W) alloys containing 25 to 35 atomic percent Re, is not specific to rhenium but is also found in alloys with other solutes from Group VIIA and the early portions of Group VIIIA. The ability of a solute to promote the rhenium ductilizing effect is related to the position of the solute in the periodic table.

The decreased hardnesses and lowered ductile-brittle transition temperatures observed in dilute Group VIA-Re alloys are attributed to the phenomenon of solution softening. This phenomenon occurs at temperatures below about 0.2 of the absolute melting point (T_m) and increases in magnitude with decreasing temperature. Although additions of rhenium are more effective than those of other Group VIIA and VIIIA elements in softening the Group VIA elements, the phenomenon is apparently present in most body-centered-cubic alloys containing small additions of substitutional solutes. The softening effect is related to a decrease in the Peierls stress on alloying.

INTRODUCTION

In 1955, Geach and Hughes (ref. 1) reported on the remarkable plasticity of Mo-35 Re and W-25Re alloys.[1] These alloys could be warm fabricated from the cast condition and finished cold, whereas unalloyed molybdenum and tungsten require hot extrusion to break down the cast structure before hot rolling.

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[1]All compositions in atomic percent.

The cold ductility of these alloys has been extensively studied by Jaffee and his co-workers (refs. 2 to 5). Both alloys are significantly more ductile than the unalloyed metals and deform initially by twinning. Klopp, et al. (ref. 6) also found that Cr-35Re is analogous to the molybdenum and tungsten alloys with respect to structure, fabricability, and cold ductility. Jaffee and his coworkers attributed the unusual behavior of these alloys to

(1) A reduction in the solubility limit for oxygen

(2) An increase in surface tension of the intergranular oxide

(3) A reduction in the stacking fault energy, resulting in easier twinning

In 1960, Robins (refs. 7 and 8) suggested that the improved ductilities were associated with decreased oxygen solubility caused by an increase in the electron-atom ratio when rhenium was added. According to this theory, the electron resonance contribution to the bond strength is at a maximum for the Group VIA elements and is in part responsible for the low interstitial solubilities in these elements. Electron-donor elements from Group VIIA (such as rhenium) and from Group VIIIA increase the electron-atom ratio and produce a corresponding decrease in the solubilities of the interstitial donor elements.

Subsequent studies conducted by Gilbert, Reid, and Hahn (ref. 9), Klein (refs. 10 and 11), Gilbert, Klein, and Edington (ref. 12), Allen (refs. 13 and 14), and Booth, Jaffee, and Salkovitz (ref. 15) were not able to establish the validity of hypotheses (1) and (2). Gilbert, el al. (ref. 9) observed larger strain aging peaks in Cr-35Re than in chromium, attributable to an increase in the amount of dissolved nitrogen. Klein (refs. 10 and 11) showed that the equilibrium solubility of nitrogen in chromium is essentially unchanged by alloying with rhenium. However, he observed that the nitride precipitation kinetics are much slower in Cr-35Re than in chromium, which allows more nitrogen to remain in solid solution and probably accounts for the large strain aging peaks. This observation, plus lack of any supporting evidence for an increase in oxygen solubility, has cast doubt on hypothesis (1). With regard to hypothesis (2), Gilbert, et al. (ref. 12) concluded that a change in grain-boundary oxide morphology is probably unimportant to the "rhenium ductilizing effect" since cracks in the Group VIA metals are frequently initiated at clean grain boundaries and propagate by intragranular cleavage, rather than intergranularly. Allen also showed (refs. 13 and 14) that rhenium has no significant effect on the surface tension of the Group VIA metals. Gilbert, et al. (ref. 12) consider important the observation that rhenium alloying changes the preferred slip plane in the Group VIA metals from {110} to {112}, since this change increases the number of available slip planes from 6 to 12 and thus increases the ease of cross-slip.

In 1964, Wukusick (ref. 16) proposed that the rhenium ductilizing effect is related to spinoidal decomposition. Specifically, he suggested that the Group VIA-Re and the Cr-20 ruthenium (Ru) alloys exhibit solute clustering with increasing solute content. The solute

2

clusters, being regions of high atomic disarray, are also sites for interstitial clustering, so that the interstitial content of the matrix is reduced. The matrix, then, being relatively free of dissolved interstitials, is more ductile. To the extent that the improved ductility is related to matrix cleanliness, the hypotheses of Wukusick and of Jaffee, et al. are similar.

More recently, Stephens and Klopp (ref. 17) proposed that the rhenium ductilizing effect is associated with the high solubility for rhenium in the Group VIA elements and the presence of an intermediate sigma phase. Sigma phase nuclei were postulated to provide stress concentration sites that could act as sources for dislocations and twins.

During the early studies of the rhenium ductilizing effect, a second rhenium phenomenon was noted. Jaffee, Sims, and Harwood (ref. 4) observed a significant hardness decrease on adding about 5 atomic percent rhenium to molybdenum. Subsequent studies by Pugh, Amra, and Hurd (ref. 18) on W-Re alloys, and by Allen and Jaffee (ref. 19) on Cr-Re alloys established that dilute alloys in these systems also exhibited lower hardness values than either the unalloyed elements or the more concentrated alloys. This phenomenon, now considered to be "solution softening,"[2] is common to most dilute substitutional body-centered-cubic alloys at low temperatures. Solution softening was shown to be associated also with decreased ductile-brittle transition temperature in dilute Mo-Re alloys by Witzke (unpublished data obtained at Lewis) and in W-Re alloys by Pugh, et al. (ref. 18) and Klopp, Witzke, and Raffo (ref. 20).

This report is a review of the properties of the Group VIA-Re alloys pertinent to both the rhenium ductilizing effect and the solution-softening effect. The properties of other alloys exhibiting similar effects are also reviewed with the view of establishing property correlations to aid in both understanding these effects and extending their ductility benefits to other systems. Areas of interest for further studies on these effects are suggested.

PROPERTIES OF GROUP VIA-RHENIUM ALLOYS

Phase Diagrams

Phase diagrams for the Cr-Re (ref. 21), Mo-Re (refs. 22 to 24), and W-Re (refs. 25 and 26) systems are presented in figure 1. These systems are similar, being character-

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[2]In the following discussions, the term "rhenium ductilizing effect" is used with reference to the effects promoted by additions of about 20 at. % or more of rhenium or rhenium analog solutes, while the term "solution softening" will be used with reference to the effects promoted by less than about 10 at. % of rhenium or of other solutes.
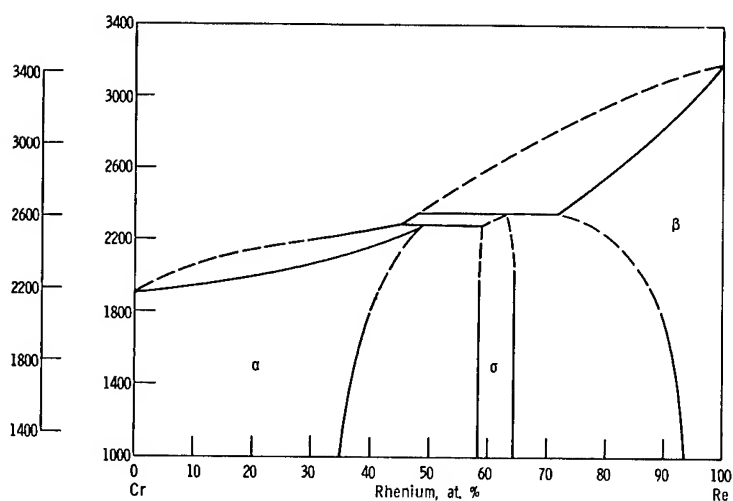
(a) Chromium-rhenium system (ref. 21).
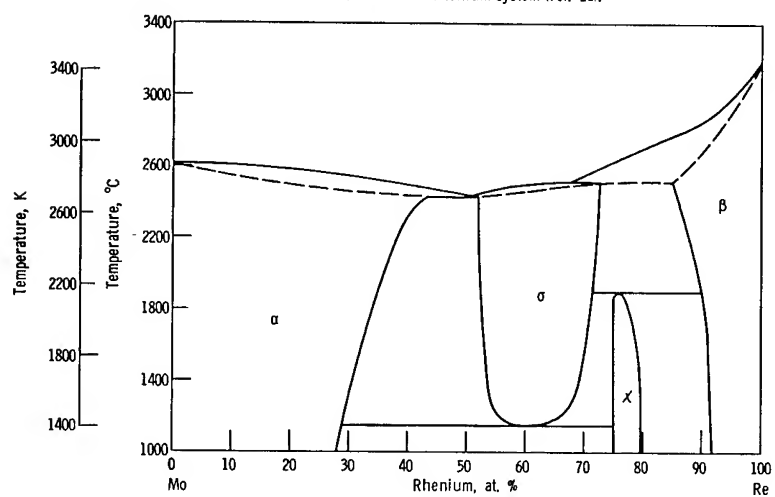
(b) Molybdenum-rhenium system (refs. 22 to 24).
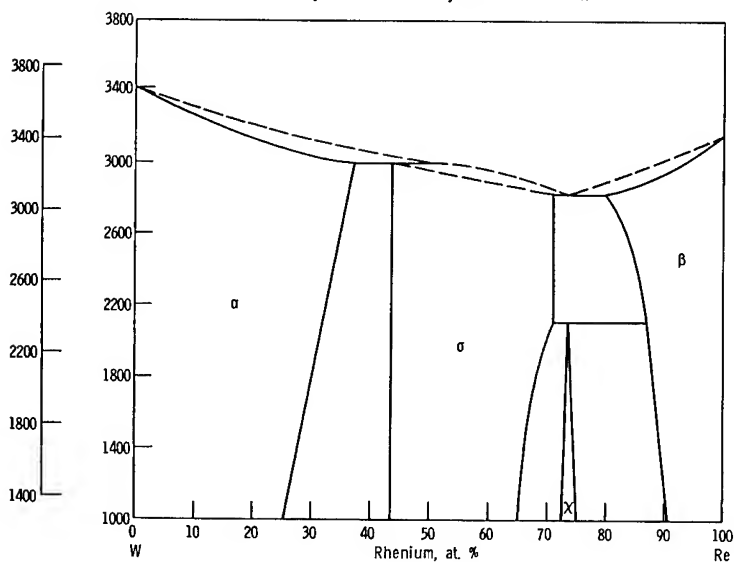
(c) Tungsten-rhenium system (refs. 25 and 26).

Figure 1. – Phase diagrams of Group VIA-rhenium systems.

4

ized by a high solubility for rhenium in the body-centered-cubic terminal phase, ranging from 37 atomic percent in tungsten to 50 atomic percent in chromium, and by the presence of an intermediate sigma phase. In addition, the Mo-Re and W-Re systems exhibit an Re_3X chi phase.

Hardness

The room-temperature hardnesses of the Group VIA-Re alloys are shown in figure 2.

The solution-softening effect is apparent in the hardness minimums at low rhenium levels in all three systems. The hardness decreases in molybdenum and tungsten are large (35 to 60 points, Vicker's hardness scale) and the minimums occur at rhenium levels of 4 to 6 atomic percent. In contrast, the hardness decrease with chromium is small (2 to 13 VHN points), while the minimum occurs at a rhenium level of 0.6 atomic percent (ref. 19). These differences in hardness behavior are attributed in part to the differences in homologous temperature at which the hardnesses were measured, since the solution-softening effect diminishes with increasing homologous temperature. Room
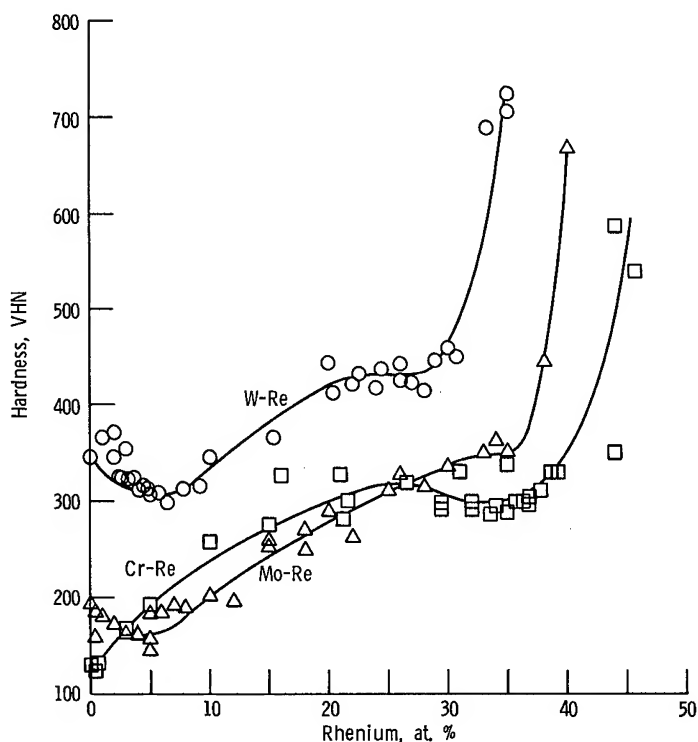

Figure 2. – Hardnesses of Group VIA-rhenium alloys at room temperature (refs. 1, 2, 4, 6, 12, 19, 20, 27, 28).

temperature is 0.14 Tm for chromium, but only 0.08 Tm for tungsten.

The rates of hardening between the initial hardness minimums and the entrance into the two-phase region are similar for all three systems, which suggests that factors other than solvent-solute atomic size considerations control solution hardening at low temperatures. At elevated temperatures, size effects may become important since dilute and intermediate W-Re and Mo-Re alloys with only a 1.4-percent size difference can be readily hot rolled (refs. 6 and 27), whereas Cr-3 to Cr-30Re alloys, with a 9.4-percent size difference, could not be hot rolled at 800° to 1033° C (1073 to 1306 K) (ref. 17.).

As the composition approaches the terminal solid solubility limit, the hardness curves flatten or decrease slightly, and a sharp rise follows associated with the appearance of the brittle sigma phase. The compositions in the hardness-plateau region exhibit the improved low-temperature ductility and twinning that are associated with the rhenium ductilizing effect.
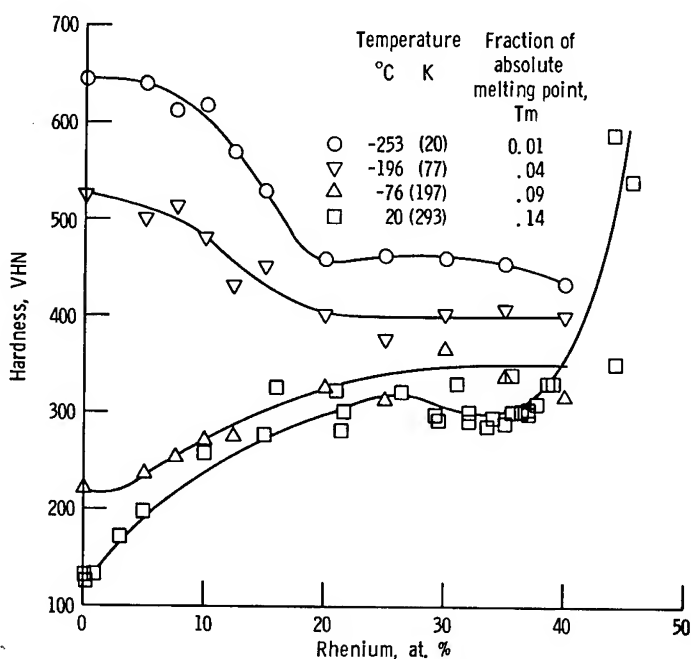
Figure 3. - Effects of temperature on hardness of chromium-rhenium alloys (refs. 6, 12, and 19).

Figure 3 illustrates the temperature dependence of the solution softening effect in Cr-Re alloys. At 20° and -76° C (293 and 197 K), the curves show the expected hardness increases with increasing rhenium content. However, at -196° and -253° C (77 and 20 K) the hardness decreases with increasing rhenium up to about 20 atomic percent after which a region of approximately constant hardness is observed. Gilbert, et al. (ref. 12)

6

also observed similar hardness trends in the Mo-Re and W-Re systems, as shown in figure 4. These hardness trends reflect the increasing magnitude of the solution-softening effect at low temperatures with regard to both the extent of the hardness decrease and the rhenium level at which the minimum hardness occurs.

Raffo (ref. 28) similarly showed that the yield stress in W-Re alloys decreases with increasing rhenium content to at least 9 atomic percent rhenium at -196° C (77 K). Low-temperature solution softening was observed also in tantalum (Ta)-Re and Ta-Mo alloys by Raffo and Mitchell (ref. 29), in iron-nickel (Fe-Ni) and Fe-platinum (Pt) alloys by
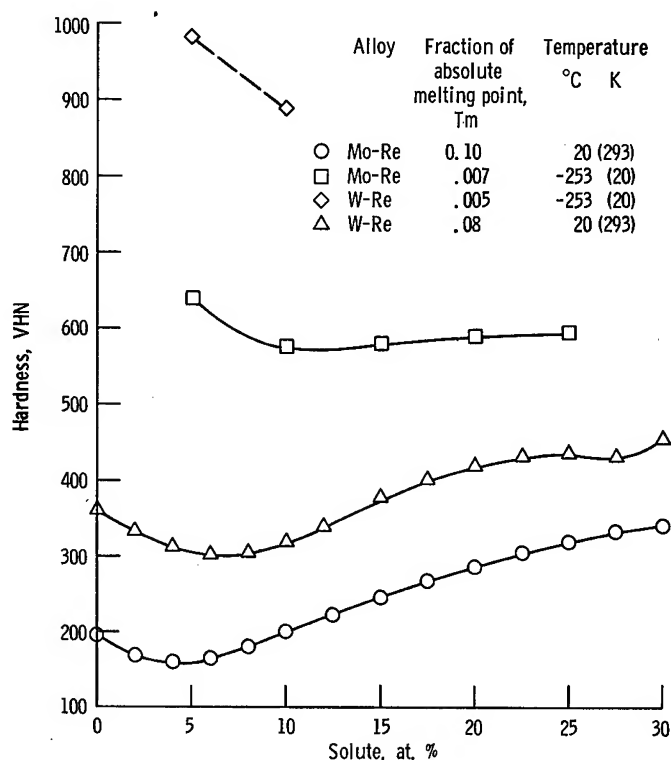
Figure 4. - Hardness curves for Mo-Re and W-Re alloys at -253° C (20 K) and 20° C (293 K) (ref. 12).

Kranzlein, Burton, and Smith (ref. 30), and in Fe-Mo alloys by Urakami, Marcus, Meshii, and Fine (ref. 31). However, in these other systems, the softening is limited to a yield strength minimum at compositions in the range of 2 to 4 atomic percent and is followed by solution strengthening at higher solute contents. Thus, the Group VIA-Re alloys appear unusual in that little strengthening or hardening occurs with increasing rhenium content at low temperatures.

Twinning

A prominent feature of the rhenium ductilizing effect (at high rhenium levels) is that initial deformation of the ductile alloys at low temperatures (less than about 0.25 Tm) is accompanied by twinning, as shown in figure 5. The importance of twinning to the rhenium ductilizing effect is not well understood, particularly since twinning accounts for only a minor fraction of the observed deformation, with slip accounting for the remainder.
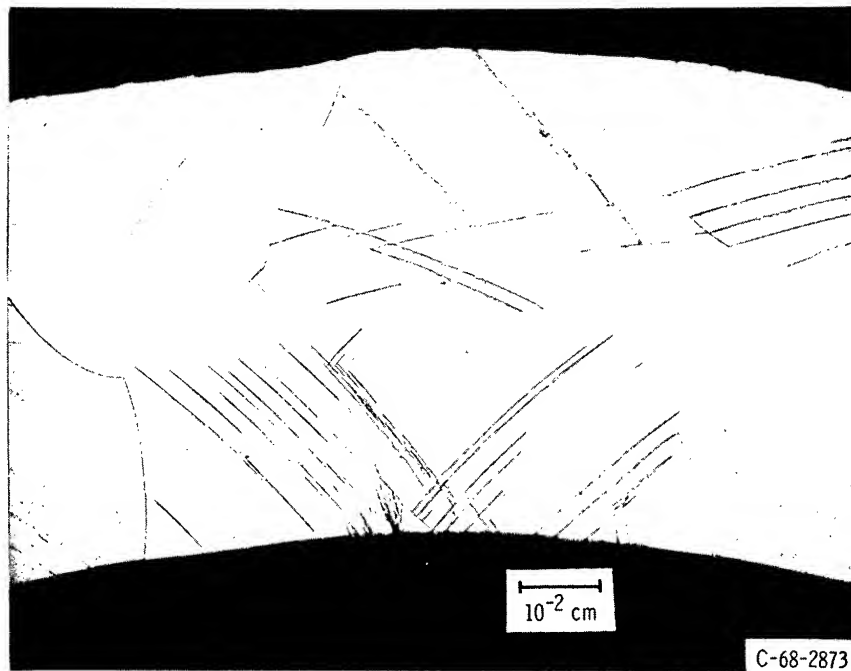
Figure 5. - Twinning in bent tungsten - 24-atomic-percent rhenium (unpublished data obtained by W. R. Witzke of Lewis).

The effects of composition on twinning are shown in figure 6 for the Cr-Re system. The temperature at which twinning is observed around a hardness impression increases sharply with increasing rhenium content above 15 atomic percent. Similar relations probably hold for Mo-Re and W-Re alloys, as well, although the temperature-composition dependencies of twinning have not been documented quantitatively in these systems.

The occurrence of twinning in the Group VIA-Re alloys may be related to a decrease in the stacking fault energy, as suggested by the results of Votava for Mo-35Re (ref. 32) and by Aqua and Wagner for W-20Re (ref. 33). However, since the twinning strain by itself can account for only a small fraction of the observed ductility, and in

Figure 6. - Temperature-composition relation for twinning around hardness impressions in cast, homogenized chromium-rhenium alloy buttons (from ref. 12).

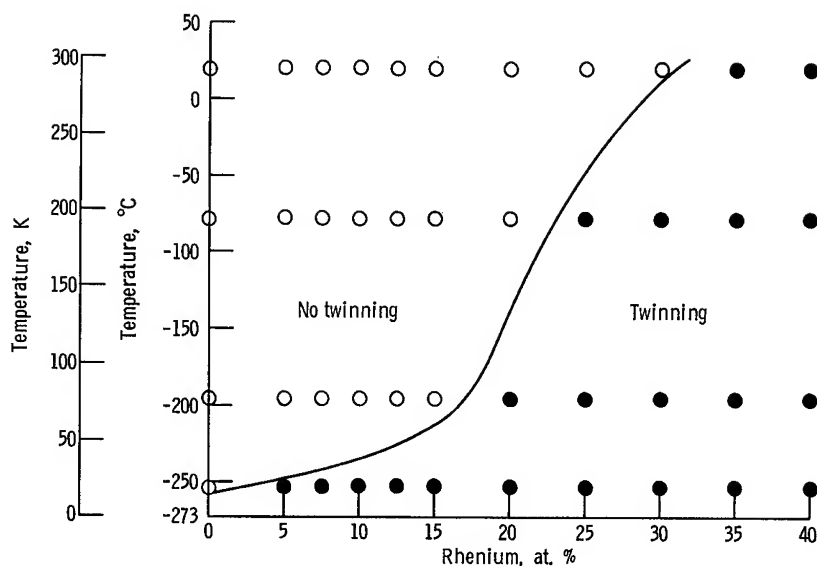view of the recent suggestion (ref. 28) that decreased stacking fault energy can also lead to easier deformation by slip in body-centered-cubic alloys, it now appears possible that twinning is associated with, but is not necessary to, the rhenium ductilizing effect.

Ductile-Brittle Transition Behavior

The small amount of data available for Cr-Re alloys indicate that the bend ductile-brittle transition temperature is reduced from 150° C (423 K) for recrystallized unalloyed chromium to about -196° C (77 K) for Cr-35Re to Cr-40Re (refs. 6 and 17). A decrease in the ductile-brittle transition temperature relative to unalloyed Cr was also observed by Carlson, Sherwood, and Schmidt (ref. 34) for a Cr-0.03Re alloy under slow bending conditions where the ductile-brittle transition temperature of unalloyed chromium was -40° C (233 K). This decrease under low-temperature testing conditions reflects the temperature dependency of the solution-softening effect.

Rhenium additions to molybdenum progressively reduce the transition temperature in the recrystallized condition, as shown in figure 7(a). A smaller decrease in the transition temperature with increased rhenium content is apparent in worked Mo-Re alloys. Note that the Mo-35Re alloy is ductile to a lower temperature in the recrystallized than in the worked condition. Unpublished data (obtained by W. R. Witzke of Lewis) also indicate a decrease in the ductile-brittle transition temperature relative to unalloyed molybdenum for an electron-beam-melted Mo-4Re alloy.

9

(a) Arc-melted molybdenum-rhenium alloys (ref. 6).
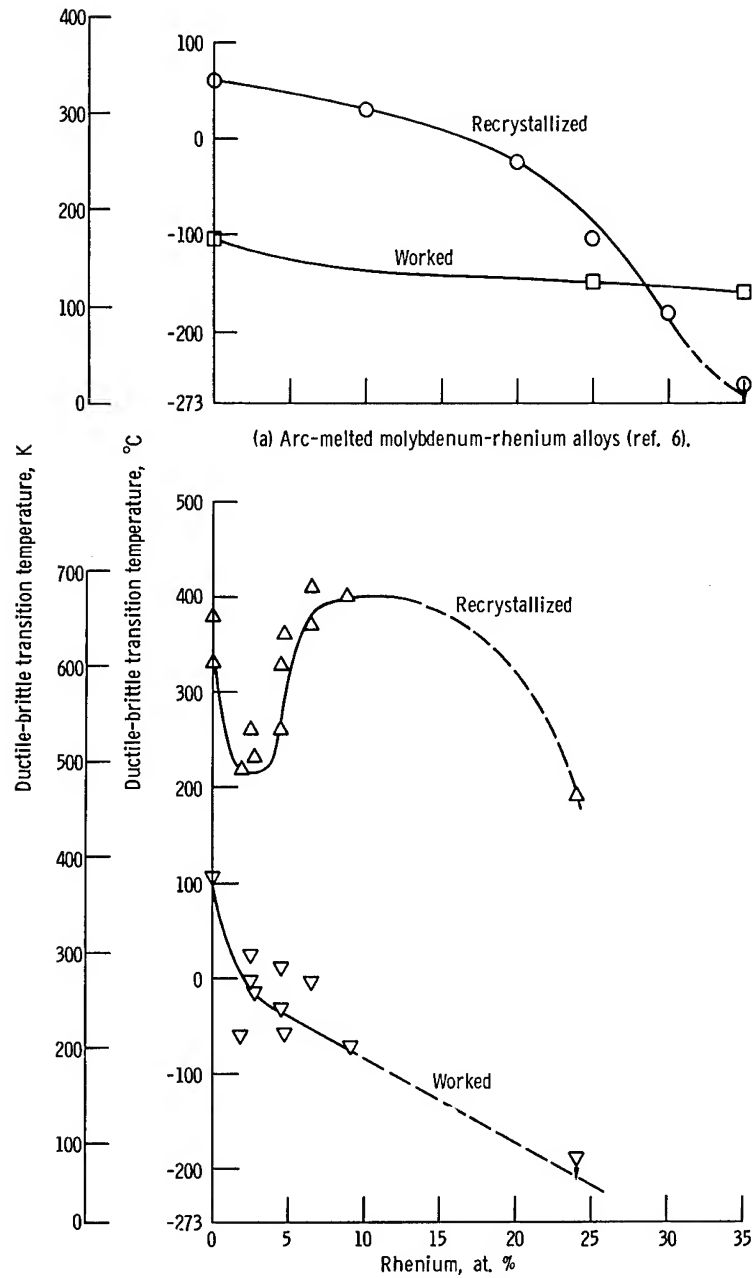
(b) Electron-beam-melted tungsten-rhenium alloys (ref. 20).

Figure 7. - Ductile-brittle bend transition temperatures for molybdenum-rhenium and tungsten-rhenium alloys.

10

For the recrystallized W-24Re alloy, the improvement in the transition temperature relative to the unalloyed metal is less than in the Cr-Re or Mo-Re system, possibly reflecting the lower solubility for rhenium in tungsten than in the other two Group VIA metals. In contrast to Mo-Re, the W-26Re alloy can be bent at much lower temperatures in the worked condition than in the recrystallized condition.

The effect of grain size on the ductile-brittle transition temperature of W-Re alloys is shown in figure 8. The grain size effect in W-24Re and W-26Re is similar to that observed by Seigle and Dickinson (ref. 35) for unalloyed tungsten. At similar grain sizes, the alloys are ductile to about 140° C (413 K) lower than unalloyed tungsten.
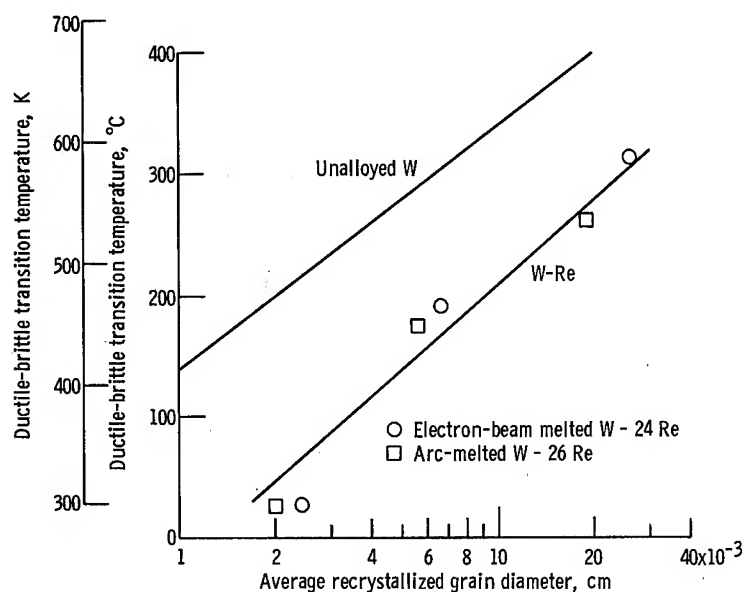
Figure 8. - Bend transition temperature for recrystallized tungsten (ref. 35) and tungsten-rhenium (ref. 20 and unpublished work of W. R. Witzke of Lewis) as function of grain size.

High-Temperature Properties

It has recently been shown by Garfinkle, et al. (ref. 27) that W-Re alloys exhibit superplasticity at elevated temperatures for compositions near the solvus line. The most prominent feature of this phenomenon is the increase in tensile elongation with increasing rhenium content at 2000° C (2273 K) (fig. 9). At this temperature, the W-25 Re alloy exhibited more than 180 percent elongation in a tensile test. The proximity of the elongation peak to the solvus line is consistent with previous observations in super-plastic systems, as described by Underwood (ref. 36) and by Weiss (ref. 37).

11

Figure 9. - Tensile elongations of electron-beam-melted tungsten-rhenium alloys annealed for 1 hour at 2300° C (2573 K) (ref. 27).

PROPERTIES OF GROUP VIA-RHENIUM ANALOG ALLOYS

During the last few years, numerous attempts have been made to duplicate the rhenium ductilizing effect in Group VIA metals using alloying elements other th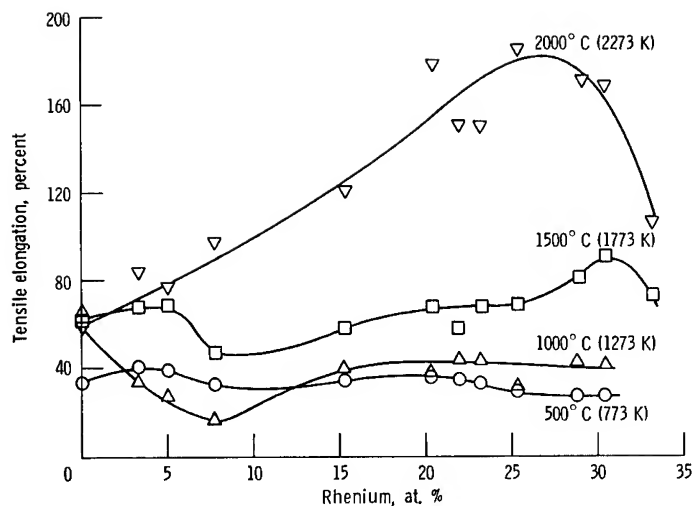an rhenium. These potential rhenium analogs have generally been located in Groups VIIA and VIIIA of the periodic table, shown in table I. The purpose of such studies has been to gain a better understanding of the mechanisms of the effect and, if possible, to reproduce the effect with alloy additions less expensive than rhenium. The selection of alloying additions and the levels studied have been based on several criteria, including similarities in electron to atom ratios and phase diagrams. The properties of the various potential rhenium-analog systems studied are discussed in the following sections.

TABLE I. - PARTIAL PERIODIC TABLE

	Group VIA	Group VIIA	Group VIIIA		
Fourth period	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.94	28 **Ni** 58.71
Fifth period	42 **Mo** 95.95	43 **Tc** (99)	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.4
Sixth period	74 **W** 183.86	75 **Re** 186.22	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.09
Number of s and d electrons	6	7	8	9	10

12

Chromium Alloys

Several studies were conducted on chromium-base systems, both at dilute (refs. 17, 19, 34, 38, and 39) and concentrated alloying levels (refs. 16, 17, 19, 38, 40, and 41). The concensus of these studies is that there are probably five solutes which can be considered as analogs to rhenium in chromium with respect to the rhenium ductilizing effect. These solutes are cobalt (Co), Fe, manganese (Mn), osmium (Os), and Ru. Technetium (Tc) is also a potential rhenium analog, although Cr-Tc alloys have not been studied.

Phase diagrams. - Phase diagrams for Cr-Co, Cr-Fe, Cr-Mn, and Cr-Ru systems are shown in figure 10. All four systems have three features in common: (1) the solute is from Group VIIA or VIIIA; (2) the solute has a high maximum solubility in chromium; and (3) the system contains an intermediate sigma phase. These features are also common to all three Group VIA-Re systems.

Hardness. - Hardness data for Cr-Re and the five systems which appear analogous to Cr-Re are presented in figure 11 (refs. 17, 19, 38, and 42). An important observation is that the solution-hardening rates, which can be represented as parabolic functions of composition, are a function of the position of the solute in the periodic table (ref. 17). Rhenium and manganese, from Group VIIA, harden chromium at a similar rate up to about 25 atomic percent solute, while iron, ruthenium, and osmium, from the first series in Group VIIIA, also have a common but higher hardening rate. Cobalt, from the second series in Group VIIIA, has the highest hardening rate of these six solutes in chromium. The hardening rates of these and other Group VIIIA solutes are given in table II. The trend for increasing hardening rates with increasing number of s and d electrons suggests that electronic interactions dominate the solution-hardening rates at low temperatures.

A second point of interest from figure 11 is that all six solutes promote a hardness decrease in chromium at high alloying levels. In the alloys of chromium with osmium, ruthenium, cobalt, and rhenium, this softening occurs at compositions slightly less than the solubility limit; in the Cr-Fe and Cr-Mn systems, softening occurs above 25 or 40 atomic percent solute, respectively, well below the maximum solubilities of these systems. These hardness decreases are correlated approximately with the onset of mechanical twinning.

It is also shown in table II that solution softening is promoted by dilute additions, less than 1 atomic percent solute, of these six solutes. This softening was studied by Allen and Jaffee (ref. 19) and was shown to occur in chromium with dilute additions of all Group IVA, VA, VIA, VIIA, and VIIIA elements. The solute contents at the hardness
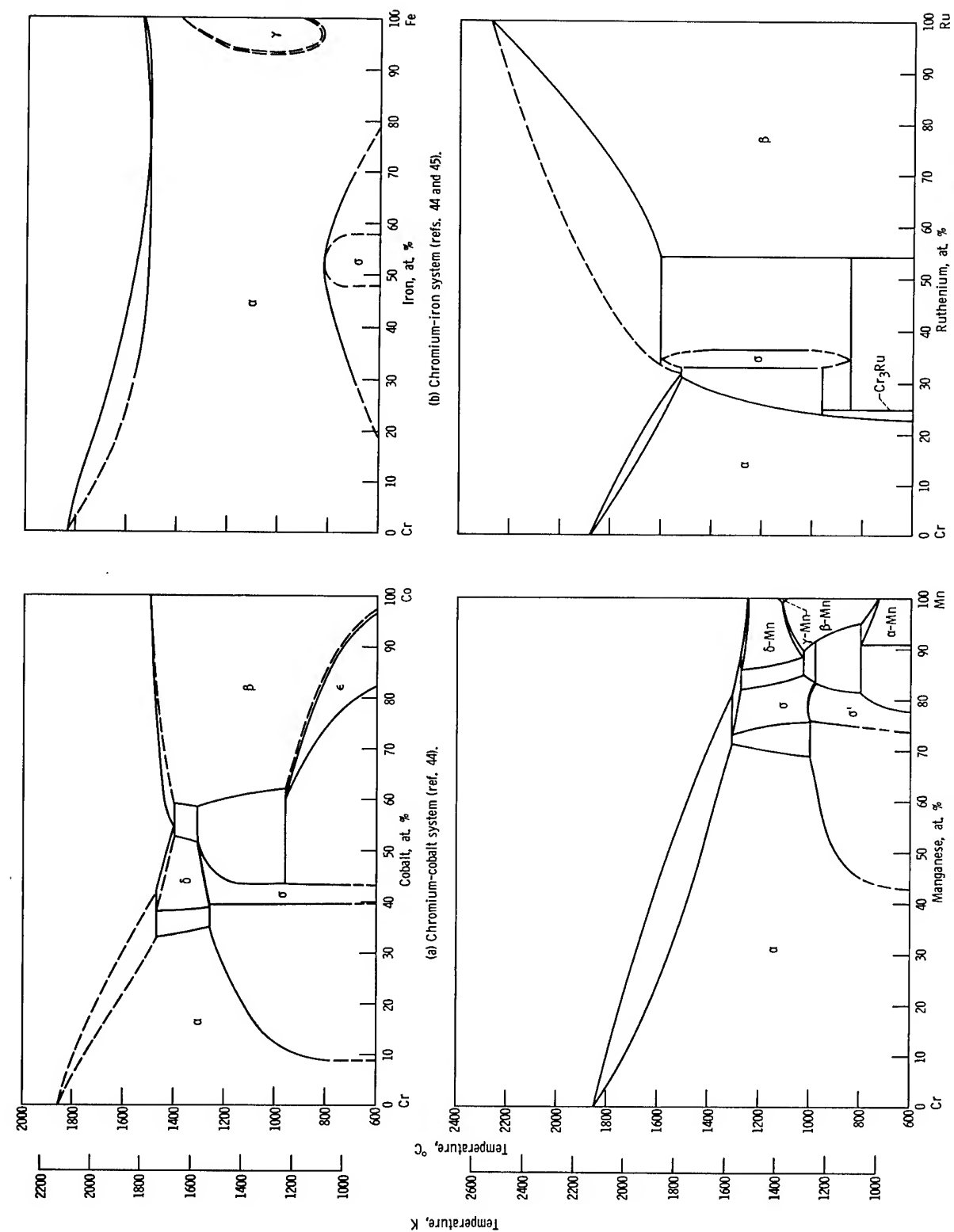
Figure 10. – Phase diagrams of chromium-base systems.

(a) Chromium-cobalt system (ref. 44).

(b) Chromium-iron system (refs. 44 and 45).

(c) Chromium-manganese system (refs. 44 and 45).

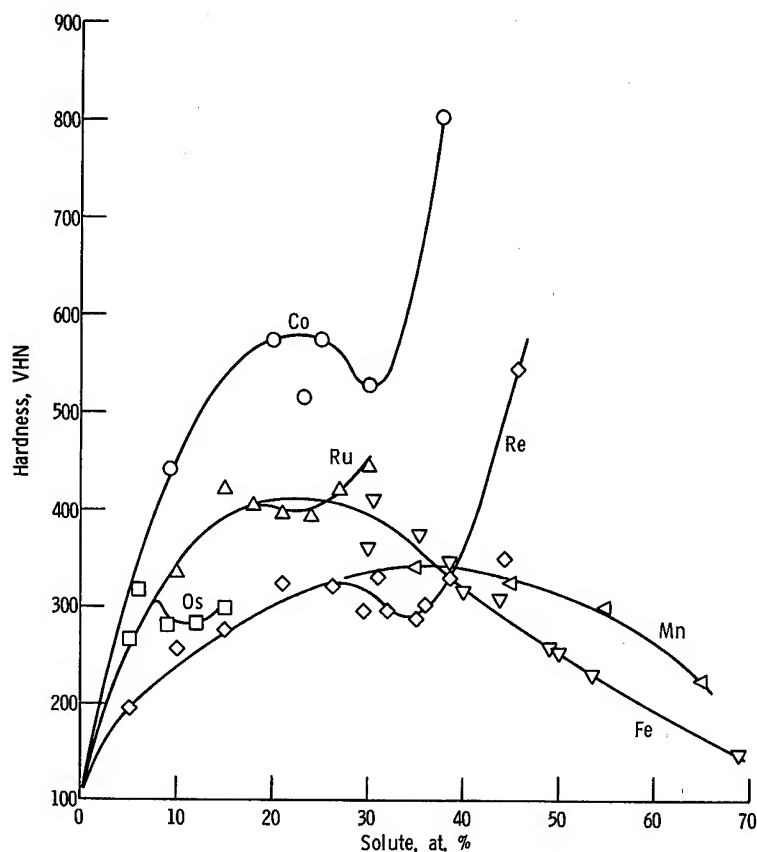(d) Chromium-ruthenium system (refs. 40 and 45).

14

Figure 11. - Hardness of chromium alloy systems (refs. 17, 19, 38, and 42).

minimums were lower for Group VIIIA than for Group VIIA elements and tended to decrease with increasing number of s and d electrons in the solute. The small amount of softening and the low solute concentrations at which the softening is found relative to rhenium in molybdenum and tungsten reflect in part the high homologous temperature of chromium at room temperature, 0.14 Tm. In contrast, room temperature is equivalent to 0.10 Tm for molybdenum and 0.08 Tm for tungsten.

Twinning. - Mechanical twinning has been observed in four of the five apparent rhenium analog systems with chromium. The solute levels in atomic percent for twinning are as follows: 26 to 63 Mn; 19 to 51 Fe; 18 to 25.5 Ru; and 30 Co (refs. 17, 19, 28, 38, and 40). In all cases, the twins were mechanical, that is, observed near hardness impressions or in deformed bend specimens, and were similar to those observed in the Cr-Re, Mo-Re, and W-Re alloys. Twins were not observed in alloys with 6 to 15 Os (ref. 17).

TABLE II. - HARDENING BEHAVIOR OF GROUPS VIIA AND VIIIA

SOLUTES IN CHROMIUM AND MOLYBDENUM

Solute	Number of s and d electrons in solute	Hardening rate[a]		Location of hardness minimum, at. % solute	Location of ductile-brittle transition temperature, at. % solute
		$\dfrac{\Delta(VHN)}{C^{1/2}}$	$\dfrac{\Delta(VHN)}{(VHN\ base)(C^{1/2})}$		
Chromium-base alloys[b]					
Mn	7	48	0.37	0.5	1
Re	7	49	.38	.6	.05
Fe	8	92	.71	.6	0
Ru	8	92	.71	.4	.6
Os	8	92	.71	.5	.5
Co	9	129	.99	.1	0
Rh	9	170	1.31	.1	.14
Ir	9	158	1.22	.1	.3
Ni	10	196	1.51	.1	0
Pd	10	344	2.65	.1	.06
Pt	10	242	1.86	.1	.1
Molybdenum-base alloys					
Re	7	59	0.31	4.5	----
Fe	8	138	.73	.11	----
Ru	8	144	.76	.25	----
Os	8	136	.72	.58	----
Co	9	242	1.27	.10	----
Rh	9	145	.76	.14	----
Ir	9	227	1.19	.20	----
Ni	10	339	1.78	.05	----
Pt	10	245	1.29	.14	----

[a]C indicates solute concentration, at. %; VHN base is 130 for Cr, 190 for Mo.
[b]Data for Cr are from ref. 19.

Ductile-brittle transition behavior. - The bend transition temperatures for Cr-Re and the five other chromium systems under discussion are shown in figure 12. Substantial decreases in the ductile-brittle transition temperatures are evident in the concentrated Cr-Ru, Cr-Co, and Cr-Fe alloys. In the Cr-Co and Cr-Fe alloys, quenching after annealing was required in order to prevent sigma precipitation, which raises the transition temperature. Although improved bend ductility has not yet been documented for Cr-Os alloys, Wukusick (private communication, June, 1967) was able to cold roll a chill-cast Cr-22Os alloy, suggesting that osmium is a rhenium analog in chromium.

No improvement in the ductile-brittle transition temperature of chromium by dilute alloying was observed by Stephens and Klopp (ref. 17). However, Carlson, et al. (ref. 34), by bending chromium slowly under conditions where the unalloyed form has a transition temperature of -40° C (233 K), observed substantial transition temperature decreases on dilute alloying of chromium with most of the elements from Groups VA, VIA, VIIA, VIIIA, and IB. The observations of improved ductile-brittle transition tem- under low-temperature testing conditions and no improvement under higher temperature testing conditions reflect the temperature dependency of the solution-softening effect.

The estimated solute contents for minimum ductile-brittle transition temperature from the work of Carlson, et al. are given in table II. The locations of the minimums are similar to the locations of the hardness minimums, both tending to decrease with in-
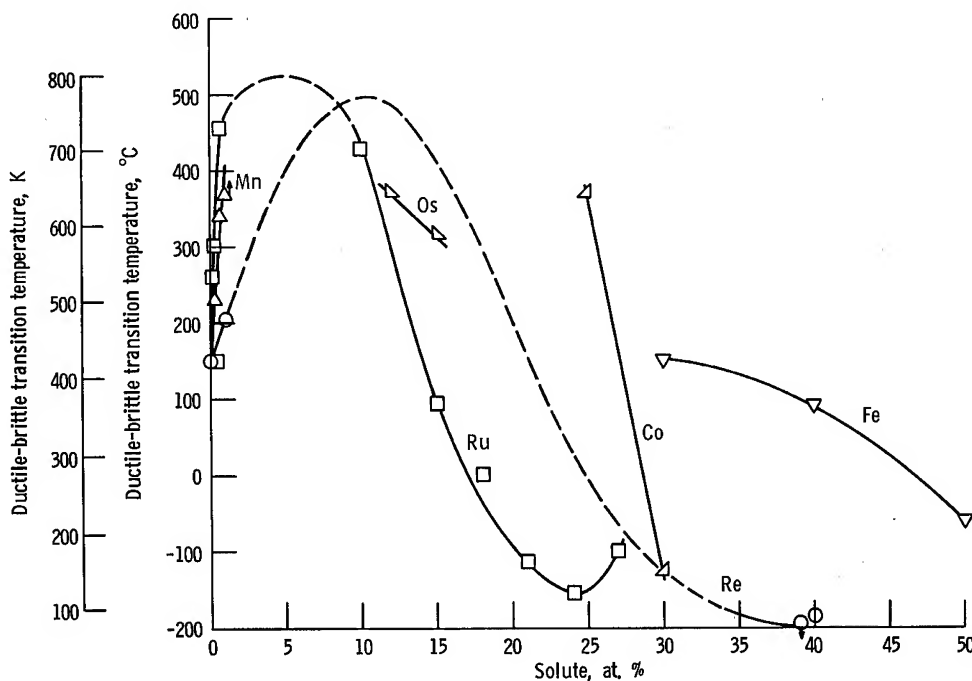

Figure 12. - Ductile-brittle transition temperatures for chromium alloys in recrystallized and quenched condition (4T bend radius) (ref. 17).

creasing number of s and d electrons in the solute. It is also noted that the solute content at the transition temperature minimum tends to increase with increasing period number of the solute for solutes in the same periodic group.

High-temperature properties. - Unusually high tensile elongations have recently been reported for near-saturated single-phase alloys in the Cr-Co and Cr-Ru systems by Stephens and Klopp (refs. 17 and 43). While these elongations (up to 160 percent) are low compared with those reported for superplastic materials, the trends are similar to those observed for W-Re alloys.

These observations suggest that high tensile elongations at elevated temperatures are another common characteristic of alloys exhibiting the rhenium ductilizing effect.

Molybdenum Alloys

Several molybdenum-base systems have been studied with respect to the rhenium ductilizing effect by Klopp, et al. (ref. 38). Although improved fabricability was promoted by a number of solutes, no improvements in the bend transition temperatures were observed.

Phase diagrams. - On the basis of the phase relations suggested by Stephens and Klopp (ref. 17), five solutes appear as potential rhenium analogs in Mo, namely, manganese, technetium, iron, ruthenium, and osmium. These five elements are from Groups VIIA and VIIIA, form an intermediate sigma phase with molybdenum, and have moderately high solubilities in molybdenum, ranging from 17 atomic percent for osmium to 30.5 atomic percent for ruthenium (refs. 44 and 45). Cobalt, which promotes the rhenium ductilizing effect in chromium, is not expected to be a rhenium analog in molybdenum because of its low solubility, 4.4 atomic percent.

Hardness. - Hardness curves for molybdenum with rhenium, ruthenium, osmium, and cobalt are presented in figure 13 (refs. 1, 2, 4, 38, and 46). The hardening trends are similar to those observed for chromium base alloys in that (1) the curves can be partially represented as parabolic functions of composition, (2) hardness minimums are observed at low alloying levels, and (3) discontinuities are apparent in the hardness curves of Mo-Ru and Mo-Os as the solubility limits are approached. The hardening rates and locations of the minimums are given in table II.

The hardening rates of Groups VIIA and VIIIA elements in molybdenum and chromium are similar when divided by the hardnesses of the unalloyed solvents to eliminate effects due to the differences in moduli and homologous temperature of measurement. These homologous hardening rates are summarized in table II, and the average hardening rates for each series of solutes are plotted in figure 14 as a function of the number of s and d electrons in the solute, that is, the position of the solute in the periodic table. Although
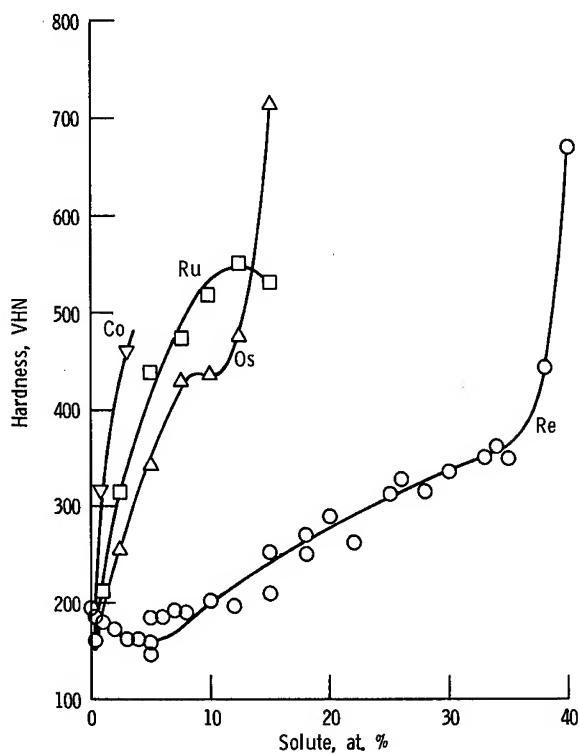
18

Figure 13. - Hardness of molybdenum-base alloys (refs. 1, 2, 4, 38, and 46).
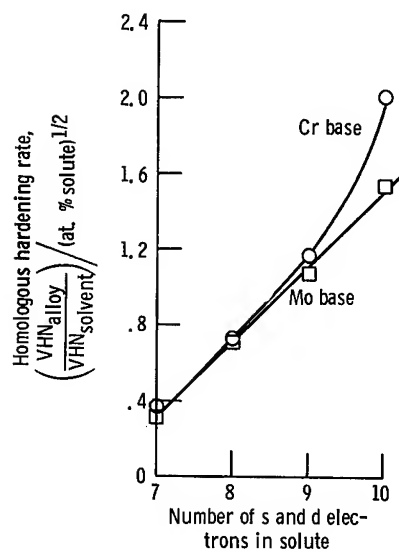

Figure 14. - Average hardening rates for Groups VIIA and VIIIA solutes in chromium and molybdenum.

the hardening rates for the individual solutes given in table II show considerable scatter, particularly for the cobalt and nickel series, the plot of average rates indicates that hardening is primarily a function of periodic position of the solute for both molybdenum and chromium alloys. Size effects are not apparent in these data.

The locations of the hardness minimums in molybdenum alloys, estimated as one-half of the solute content at the point where the hardness was equal to that of unalloyed molybdenum, are presented in table II and figure 15. The figure indicates that the solute content of the minimum decreases rapidly as the number of s and d electrons in the solute increases from 7 to 10 and also that the solute content is highest for the sixth period elements and least for the fourth period elements. These trends are similar to those observed for chromium alloys and indicate that the location of the hardness minimum is also related to the periodic position of the solute.

Twinning. - Twinning has been observed near room-temperature hardness impressions in alloys from several molybdenum systems, including Mo-Ru, Mo-Os, Mo-rhodium (Rh), Mo-iridium (Ir), and Mo-Pt (ref. 38). The minimum alloying level for twinning in these systems was 5 atomic percent. Twinning was also observed by Baird, et al. (ref. 47) during room-temperature rolling of a Mo-14Os alloy.

Fabricability and ductility. - Improved fabricability has been noted for molybdenum alloyed with several solutes from Groups VIIA and VIIIA. Specifically, cast button ingots containing the following solutes, in atomic percent, could be warm rolled at 800° to 1000° C
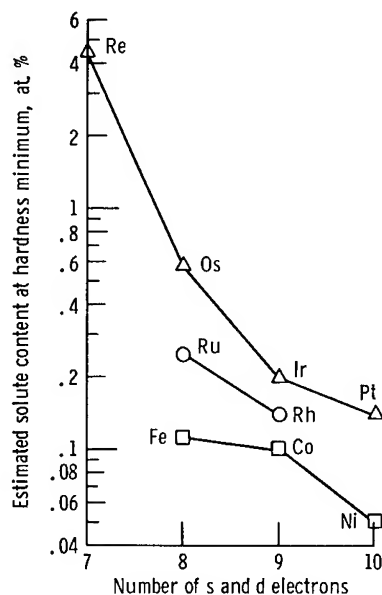

Figure 15. - Locations of hardness minimums in molybdenum-base alloys (from data in refs. 38 and 46).

(1073 to 1273 K); 0.1 and 1 Ru, 0.1 to 7.5 Os; 0.1 Co; 0.1 and 0.5 Rh; 1 Ir; and 0.1 and 0.5 palladium (Pd) (ref. 38). Baird, et al. (ref. 47) were able to fabricate a Mo-14Os alloy to almost 50 percent reduction at room temperature. In contrast, similar button ingots of unalloyed molybdenum could not be rolled at 1400° C (1673 K). The relatively extended range for warm fabricability of the Mo-Os alloys is associated with both the lower number of s and d electrons compared with cobalt, rhodium, iridium, and palladium, and with a better solvent-solute size fit with Mo-Os than with Mo-Ru. The cold fabricability of Mo-14Os suggests that this alloy is a true rhenium analog.

The bend transition temperatures for fabricable molybdenum alloys with Group VIIIA solutes are shown in figure 16. None of these solutes decreased the transition temperature of molybdenum, in contrast to the results achieved with chromium base alloys.
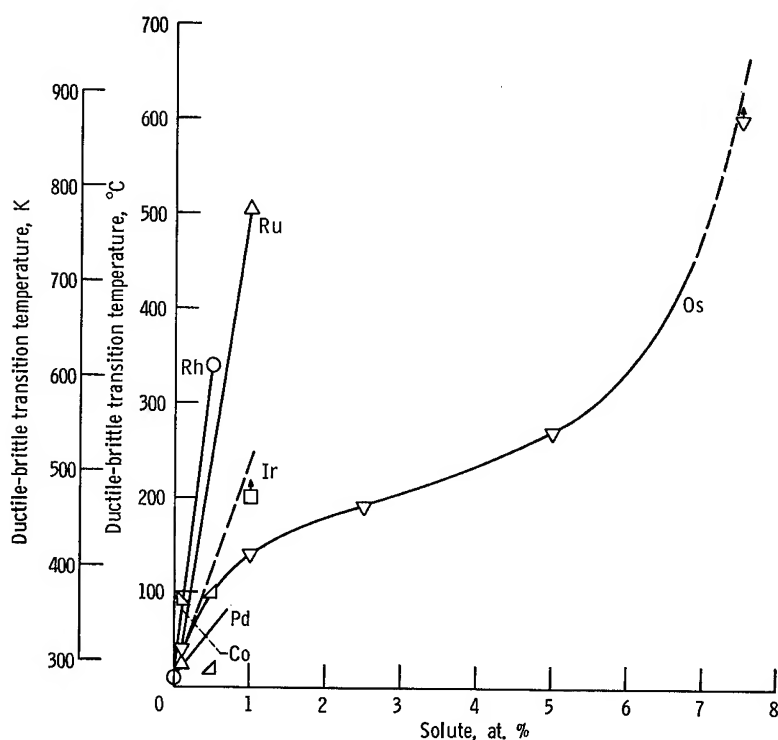
Figure 16. - Ductile-brittle transition temperatures for molybdenum-Group VIIIA alloys (1.5 T bend radius) (ref. 38).

Tungsten Alloys

No rhenium analogs in tungsten have been identified. The properties of several potential analogs are reviewed in this section.

Phase diagrams. - A review of the available phase diagrams and information (refs. 44, 45, and 48) indicates that technetium and rhenium from Group VIIA have high solubilities in tungsten (48 and 37 at. %, respectively), while ruthenium and osmium from

Group VIIIA have intermediate solubilities in tungsten (23 and 18.5 at. %, respectively). Sigma phases are also present in all four of these systems. The solubilities of the other Group VIIIA elements in tungsten are low, ranging from 0.9 atomic percent for cobalt and nickel to between 3.8 and 5.7 atomic percent for platinum. Sigma phases have been identified in the W-Co and W-Ir systems. It would be expected from these phase relations that technetium is a probable rhenium analog in tungsten, while ruthenium and osmium are possible but doubtful.

Hardness. - The hardness curves for tungsten alloyed with technetium, rhenium, ruthenium, and osmium are shown in figure 17. The hardening rates of ruthenium and
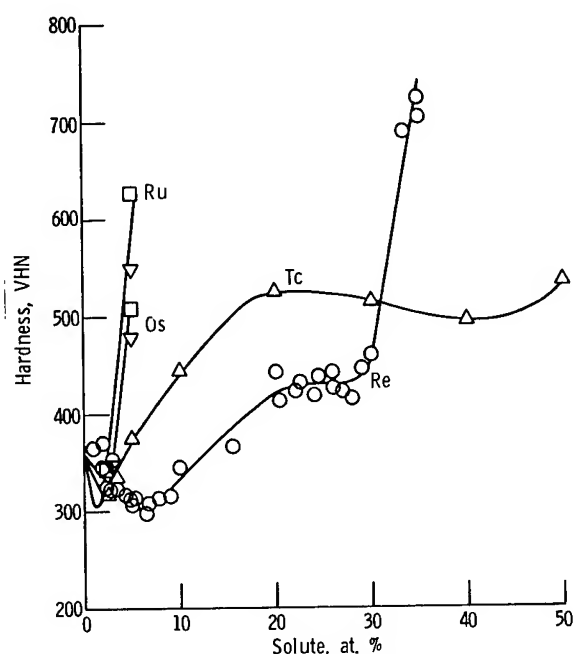

Figure 17. - Hardness of tungsten-base alloys (refs. 4, 19, 20, 28, 38, and 48).

osmium in tungsten are significantly greater than those of technetium and rhenium, further indicating that the hardening rates increase with increasing number of s and d electrons, as shown for chromium and molybdenum alloys (fig. 14).

Substantial hardness decreases associated with solution softening are observed at low alloying levels. The solute contents at these minimums follow the trends exhibited by chromium and molybdenum alloys, decreasing with increasing number of s and d electrons and increasing with increasing period number. These data are shown in figure 18. The solute contents at the hardness minimums are greater than those for similar chromium or molybdenum alloys, reflecting the lower homologous temperature which room temperature represents in tungsten.
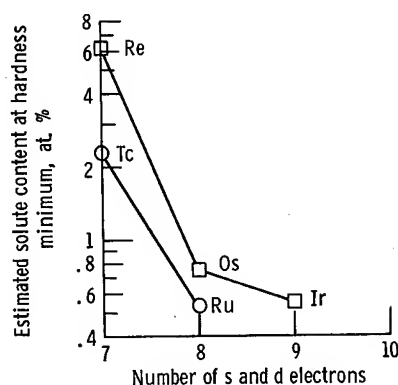
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Figure 18. - Locations of hardness minimums in tungsten-base alloys (from data in refs. 4, 19, 20, 28, 38, and 48).

Fabricability. - The W-Tc alloys possess some degree of fabricability. Kemper and Keefe (ref. 49) observed that alloys containing 2.5 to 40 Tc could be press-forged to 60 percent reduction at 1700° C (1973 K) with only minor edge cracking, while alloys with 50 and 60 Tc cracked, presumably because of the presence of the brittle sigma phase.

DISCUSSION

Rhenium Ductilizing Effect

As indicated in the foregoing sections, several rhenium analogs, which promote decreased ductile-brittle transition temperature and twinning at high solute contents, have now been identified for chromium and are probable for molybdenum and tungsten. These analog solutes are located in Group VIIA and the early portions of Group VIIIA (see table I).

In chromium, the known analogs include iron, ruthenium, and cobalt, while manganese, technetium, and osmium are probable. In molybdenum, no analogs are known, but technetium and osmium are probable and manganese, iron, and ruthenium appear possible. In tungsten, technetium is a probable rhenium analog, and ruthenium and osmium appear possible. The identification of these suggested analogs is based on phase-diagram considerations, hardening rates, and propensity for twinning, all of which are related to the position of the solute in the periodic table.

Examination of the phase diagrams for the six systems known to exhibit the rhenium ductilizing effect, Cr-Re, Mo-Re, W-Re, Cr-Fe, Cr-Ru, and Cr-Co, indicates two

major common features. These features are a high solubility for the solute in chromium, molybdenum, or tungsten, and the presence of an intermediate sigma phase.

Phase diagrams for chromium, molybdenum and tungsten with the Groups VIIA and VIIIA elements indicate two trends regarding solubility. The major trend is for decreasing solubility with increasing number of s and d electrons. This trend is consistent with the theory of Robins (refs. 7 and 8) which predicts decreasing solubility as the average electron-atom ratio is increased above 6. An analysis of the solubility trends shown in figure 19 indicates that the solubilities vary as $1/V^2$, where V is the number of s and d electrons in the solute minus 6. Thus, the group manganese, technetium, and rhenium have the highest solubilities in chromium, molybdenum, and tungsten, while nickel, palladium, and platinum tend to have the least. A minor trend is noted for solutes to have the highest solubility in the Group VIA element from the same period. Further analyses of the solubility data for the individual systems revealed no consistent variation of solubility with atomic misfit parameters or with the solvent or solute elastic moduli.

Sigma phases have been identified in the Group VIA systems with most of the elements from the groups headed by Mn and Fe and some from the group headed by cobalt. The six possible rhenium analogs in chromium, five in molybdenum, and three in tungsten, listed previously, are the only solutes known or expected (in the case of technetium) to meet the criteria of having a solubility of at least 20 atomic percent and forming a sigma phase with chromium, molybdenum, or tungsten.
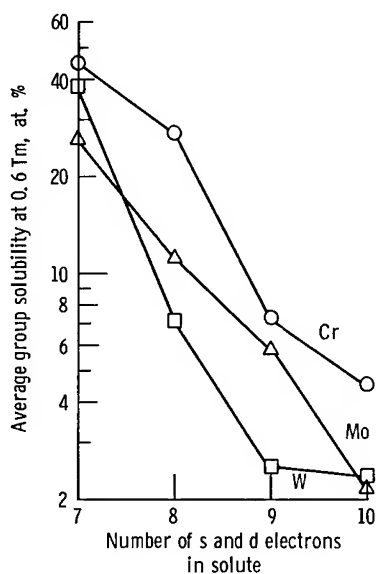
Figure 19. – Average solubilities of Groups VIIA and VIIIA elements in chromium, molybdenum, and tungsten at 0.6 Tm.

The hardening rates for all the Group VIIA and VIIIA solutes in chromium, molybdenum, and tungsten increase rather sharply with increasing number of s and d electrons, as shown for chromium and molybdenum systems in figure 14 and table II. This consideration appears important, since the absolute hardness of a material governs its ductility to some extent. For example, Cr-35Re and Mo-35Re are both softer (fig. 2) and have lower ductile-brittle transition temperatures (fig. 7) than W-25Re. On this general basis, solutes from Group VIIA and the early portions of Group VIIIA are more probable rhenium analogs than solutes from the later portions of Group VIIIA.

The effectiveness of solutes in promoting twinning appears to vary with the solute relation to the solvent in a manner similar to the solubility relations described previously. Although less well documented than the solubilities or hardnesses, the solute levels for twinning are generally higher, for example, for solutes from the manganese group than for solutes from the nickel group, and are also higher for solutes from the same periodic series as the solvent. Twinning does not necessarily occur near the solubility limit; Cr-Mn and Cr-Fe alloys twin at solute levels substantially below the solubility limit (for Mn) or the sigma-phase composition (for Fe). The twinning at low temperatures in Cr-Re alloys which do not twin at room temperatures (see fig. 5) is a further indication that twinning is associated with a factor other than the impending appearance of a new phase. Twinning thus appears to be a function of temperature and of solute electronic properties similar to those which govern solubility rather than a function of solubility itself.

Although it now appears possible to identify probable rhenium analogs for chromium, molybdenum, and tungsten, the mechanism of the rhenium ductilizing effect remains elusive. Certain conclusions, however, can be drawn from the growing body of information now available. It appears that the periodic position of the solute is of basic importance in controlling the properties of the Group VIA systems with solutes from Groups VIIA and VIIIA. This factor influences the solubility relations, appearance, and location of the sigma phase, hardening, twinning, and most likely, the improved ductility associated with the rhenium ductilizing effect. The correlations between the rhenium ductilizing effect and, for example, the phase diagrams thus reflect the probability that both are controlled by electronic features of the solute rather than being directly interrelated. The previous suggestions that grain boundary oxide distribution and interstitial solubilities are important factors in the rhenium ductilizing effect are inconsistent with the present suggestion. It is also apparent that the rhenium effect is restricted to Group VIA solvents, since the columbium (Cb)-Re and Ta-Re systems, which contain sigma phases, do not exhibit the rhenium ductilizing effect (refs. 2, 29, and 50).

The role of superplasticity in the rhenium ductilizing effect also is not clear at this time. It has, however, been observed in three systems to date (Cr-Co, Cr-Ru, and W-Re) and can be expected to be found in other systems exhibiting the rhenium ductilizing

25

effect, based on phase-relation similarities. It is possible that superplasticity is associated with the apparent solute segregation to the grain boundaries observed by Underwood in Cr-Re and Mo-Re alloys (ref. 51).

Solution Softening Effect

The phenomenon observed in dilute Group VIA-Re alloys, consisting of softening and lowered ductile-brittle transition temperature, appears to be a separate phenomen from the rhenium ductilizing effect, even though both effects are most prominent with rhenium additions. Solution softening is promoted in Group VIA solvents by solute additions from Groups VA, VIA, VIIA, and VIIIA. Additionally, it has been observed in the form of a yield strength minimum at low temperatures with body-centered-cubic solvents from other than Group VIA, such as Ta-Re, Ta-Mo, Fe-Ni, Fe-Pt, and Fe-Mo. Thus, this effect is far more widespread than the rhenium ductilizing effect. The solution-softening effect is also quite temperature dependent, disappearing at a temperature somewhat above 0.2 Tm.

Two trends in the location of the hardness and ductile-brittle transition temperature minimums are apparent for alloys of the Group VIA metals with solutes from Groups VIIA and VIIIA. The major trend is for the solute content at the minimum to decrease with increasing number of s and d electrons, while the minor trend is for the solute content to increase with increasing period number. Thus, the solute content at the minimum is expected to be highest for rhenium and least for nickel in all three Group VIA elements. These data suggest that the locations of the minimums are inversely proportional to the hardening rates at higher solute contents, which in turn appear related to the positions of the solutes in the periodic table. The inverse relation between the solute contents at the hardness minimums and the room-temperature hardening rates is shown in figure 20.

It is of interest to note that the temperature dependence of the low-rhenium effect sometimes tends to mask its detection. Thus, although the effect is present in all three Group VIA elements, it is more easily detectable by room-temperature hardness measurements in tungsten than in chromium because room temperature represents a lower homologous temperature in tungsten than in chromium, 0.08 against 0.14 Tm, respectively.

Similarly, the ductile-brittle transition temperature improvements are more pronounced under conditions allowing their measurement at low temperatures. Thus, Stephens and Klopp (ref. 17), by testing under conditions where unalloyed chromium has a ductile-brittle transition temperature of 149° C (422 K), could detect no ductility improvement in dilute alloys of chromium with rhenium, ruthenium, iridium, or manga-
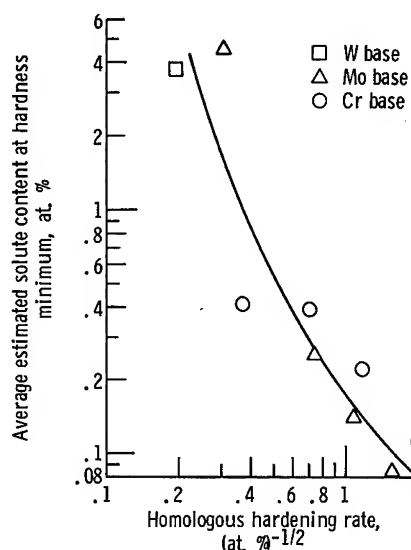
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Figure 20. – Inverse relation between location of hardness minimum and hardening rate.

nese because the solution-softening effect is minimal at this temperature. However, Carlson, et al. (ref. 34), by testing under conditions where unalloyed chromium has a transition temperature of -40° C (233 K), detected ductility improvements on dilute alloying with most of the Group VIIA and VIIIA elements.

The mechanism of solution softening, like that of the rhenium ductilizing effect, is certainly not clear at this time. However, it appears related to the temperature-dependent component of the yield stress (Peierls-Nabarro stress) at low temperatures. The large increase in the yield stress of body-centered-cubic metals at temperatures below 0.2 Tm is well known and consists of a temperature-independent component which is increased by alloying and the Peierls-Nabarro stress component, which is decreased by alloying. The decrease in the Peierls-Nabarro stress effected by dilute alloying increases the mobility of screw dislocations and allows plastic flow at a lower applied stress. The minimums in the yield strength-composition and hardness-composition curves at low temperatures appear to result from the addition of the Peierls-Nabarro stress curve and the temperature-independent component of the yield stress, which are affected oppositely by alloying.

Suggested Areas for Future Research

Future studies on the rhenium ductilizing effect should include the following:

1. The basis for the correlation of properties with the number of s and d electrons should be explored.

2. The potential for obtaining less expensive alloys with lower ductile-brittle transition temperatures from combinations of rhenium analogs, such as Cr-Re-Fe, and from combinations of rhenium analogs with non-rhenium analogs, such as Cr-Fe-Ni, should be investigated. Additionally, the strengthening of such ductile alloys by proper dispersions or precipitates could produce materials with improved combinations of high-temperature strength and low-temperature ductility.

Future studies on the decreased ductile-brittle transition temperatures associated with solution softening in the Group VIA metals should include:

1. The temperature and microstructural dependence of solution softening should be characterized in selected systems in order to clarify the responsible mechanism(s).

2. The effectiveness of combinations of various solutes in softening and in lowering the ductile-brittle transition temperatures of the Group VIA elements should be evaluated.

3. The feasibility of combining the solution-softening effect with various high-temperature strengthening mechanisms to produce ductile, high-strength refractory alloys should be studied.

CONCLUSIONS

The major conclusions from this review on the rhenium ductilizing effect and solution-softening effects in the Group VIA metals can be summarized as follows:

1. The "rhenium ductilizing effect" is not specific to Group VIA rhenium alloys but is found also in concentrated alloys of Group VIA metals with other solutes from Group VIIA and the early portions of Group VIIIA.

2. The ability of a solute to promote the rhenium ductilizing effect is related to the number of s and d electrons in the solute, that is, to the position of the solute in the periodic table. Rhenium analog solutes contain 7, 8, or 9 s and d electrons.

3. Rhenium analog systems have a large terminal solubility (20 at. % or greater), and contain an intermediate sigma phase.

4. Other properties of Group VIA alloys with solutes from Groups VIIA and VIIIA also are largely determined by the positions of the solutes in the periodic table. These properties include phase relations (solubilities, presence, and locations of sigma phases), low-temperature solution-hardening rates, and propensity for twinning.

5. The decreases in hardness, yield strength, and ductile-brittle transition temperature effected by additions of less than about 10 atomic percent rhenium to the Group VIA elements are associated with the phenomenon of solution softening. This phenomenon occurs with most dilute substitutional alloy additions to body-centered-cubic metals.

It is highly temperature dependent, increasing with decreasing temperature below about 0.2 Tm.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, August 8, 1968,
            129-03-02-02-22.

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